Synthesis of $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$

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RECENTLY new syntheses of $Ru_3(CO)_{12}$[1] and $Os_3(CO)_{12}$[2] have been described. Herein we report a new method for preparing $Rh_6(CO)_{16}$ and $Ir_4(CO)_{12}$, thereby making these polynuclear carbonyls readily accessible for study.

The black rhodium carbonyl formulated as $Rh_4(CO)_{11}$[3] was shown to be $Rh_6(CO)_{16}$ by *X*-ray crystallography.[4] The previous synthesis of this carbonyl involved treating dry rhodium trichloride and silver or copper with carbon monoxide at 80—230° and 200 atm.[3] Similarly, $Ir_4(CO)_{12}$ was prepared by the carbonylation of dry iridium trichloride at 140° and 350 atm. of carbon monoxide.[5]

We have prepared $Rh_6(CO)_{16}$ in 80—90% yield by treating rhodium trichloride trihydrate in methanol with carbon monoxide under mild conditions (60°/50 atm.) At 25 atm. carbon monoxide pressure, the halide $[Rh(CO)_2Cl]_2$ is formed. The hexanuclear carbonyl, $Rh_6(CO)_{16}$, separates from the reaction mixture as large black crystals [ν(CO) 2072, 2024, and 1800 cm.$^{-1}$ (in Nujol); lit.,[6] 2073, 2026, 1800 cm.$^{-1}$ (in KBr)]. Interestingly, unlike in the previous synthesis[3] or in the preparation of $Ru_3(CO)_{12}$,[1] a halogen acceptor is not required.

Under similar conditions to those which afford $Rh_6(CO)_{16}$, iridium trichloride in methanol reacts with carbon monoxide to give the tetranuclear carbonyl $Ir_4(CO)_{12}$ in 50—60% yield. The yellow product may be purified by recrystallization from cyclohexane, in which solvent it shows carbonyl stretching absorptions at 2071, 2064, and 2032 cm^{-1}.

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